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THE PREPARATION OF HIGH-PURITY ^{242}Cm
IN MULTICURIE QUANTITIES

by

E. P. Horwitz, C. A. A. Bloomquist,
and H. E. Griffin

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Chemistry Division

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I. INTRODUCTION

During the past two years the authors have been involved in the processing of irradiated ^{235}U for ^{239}Pu . The resultant ^{239}Pu was used as an alpha source in the neutron calorimetry performed by the authors on the ^{235}U target surface.¹ The ^{239}Pu employed in these studies is said to be highly decontaminated from the capsule material, free of fission products, and such additional impurities as sodium and calcium. This report describes the method presently employed for the isolation and purification of 20-30 G quantities of ^{239}Pu . The current procedure represents a significant improvement over the previous method described by the authors.

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ABSTRACT

The ^{242}Cm was prepared in 20-30-Ci quantities by neutron irradiation of 150-230 mg of $^{241}\text{AmO}_2$ encapsulated in aluminum. The irradiated capsule was dissolved in conc HNO_3 containing a Hg^{+2} catalyst. A high-molecular-weight, quaternary ammonium nitrate extractant (Aliquat-336 nitrate) in xylene was used to extract the curium and americium from the resultant $\text{Al}(\text{NO}_3)_3$ solution and also from certain fission products. The bulk of the ^{241}Am was removed from the ^{242}Cm by oxidation of the $\text{Am}(\text{III})$ to $\text{Am}(\text{V})$ in 4M K_2CO_3 . Additional decontamination of ^{241}Am from ^{242}Cm was achieved by extraction chromatography using Aliquat-336 nitrate on Celite and a LiNO_3 elutriant. Lanthanide fission products remain in the americium fraction. Final purification of the ^{242}Cm was carried out by extraction chromatography using HDEHP on Celite and a dilute nitric acid elutriant.

The final product was spectroscopically pure ($>99.9\%$) of such impurities as Na, Ca, Al, and Fe, and radiochemically pure of all fission products. The ^{241}Am was reduced to ~ 100 ppm by mass, corresponding to an alpha-activity ratio of $10^7:1$ ($^{242}\text{Cm}:^{241}\text{Am}$).

I. INTRODUCTION

During the past five years the authors have been involved in the processing of irradiated ^{241}Am for ^{242}Cm . The resultant ^{242}Cm has been used as an alpha source in the instruments which performed the chemical analysis of the lunar surface.¹ The ^{242}Cm employed in these instruments had to be highly decontaminated from the capsule material, fission products, americium, and such adventitious impurities as sodium and calcium. This report describes the current process employed for the isolation and purification of 20-30-Ci quantities of ^{242}Cm . The current process represents a considerable improvement over the previous method described by the authors.²

II. GENERAL PROCESSING APPROACH

The ^{242}Cm is prepared by neutron irradiation of 150-250-mg samples of $^{241}\text{AmO}_2$ encapsulated in high-purity aluminum. After irradiation, the two major constituents in addition to the ^{242}Cm are aluminum and americium. The quantity of fission products, by mass, is small in comparison to the quantity of ^{242}Cm , since the nvt is usually in the range of $\sim 2 \times 10^{20}$. (Nevertheless, the gamma activity from the fission products is sufficiently high that most of the processing must be performed by remote control in a high-level cave.)

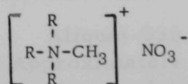
The chemical processing is divided into the following steps:

- A. dissolution of the capsule and recovery of americium and curium from the aluminum;
- B. separation of americium and curium;
- C. final purification of ^{242}Cm .

A. Dissolution of the Capsule and Recovery of Americium and Curium from the Aluminum

The aluminum capsule, containing fission products and the oxides of americium and curium, is dissolved in nitric acid. The resultant aluminum nitrate solution is evaporated, partially neutralized, and then used as a salting-out agent for the extraction of Am(III) and Cm(III) by a high-molecular-weight, quaternary ammonium nitrate (Aliquat-336 nitrate).^{*} The extraction of Am(III) and Cm(III) from various nitrate solutions by Aliquat-336 nitrate has been reported by Moore,³ van Ooyen,⁴ and the authors.⁵⁻⁷ The authors have found that high K_d values can be obtained for Am(III) and Cm(III) using a 0.4F Aliquat-336 nitrate-xylene solution and an aluminum nitrate solution in the range from 4 to 8M in nitrate and <0.1M in hydrogen ion. The separation factor between Cm(III) and aluminum is greater than 10^5 . Concentrated LiNO_3 solution is used as a scrubbing agent for additional decontamination of the curium and americium.⁵ Plutonium (IV) and lanthanide (III) ions are also highly extracted by Aliquat-336 nitrate, whereas the fission products Cs, Sr, Zr, and Nb are poorly extracted. The Cm(III) and Am(III), together with the lanthanide (III) ions, are easily stripped from the organic phase with 3M HCl. The ^{242}Cm can also be concentrated during the extraction step by adjusting the organic

*Aliquat-336 nitrate is a quaternary ammonium nitrate with the following structure:



where R is a mixture of n-octyl and n-decyl.

to aqueous phase ratio (O/A) to <1 during the feed extraction and to >1 during the stripping extraction.

B. Separation of Americium and Curium

The bulk of the ^{241}Am is separated from the ^{242}Cm by oxidation of Am(III) to Am(V) with OCl^- in 4M K_2CO_3 , followed by precipitation of the slightly soluble KAmO_2CO_3 .² However, one oxidation cycle does not give adequate decontamination of the ^{241}Am from the ^{242}Cm . In order to reduce the ^{241}Am concentration in ^{242}Cm to less than 1% by mass, an extraction chromatography procedure is employed.^{6,7} By means of this procedure the Am-Cm separation is accomplished using a column containing Aliquat-336 $\cdot\text{NO}_3$ adsorbed on Celite and a concentrated LiNO_3 solution as the elutriant. The separation factors (Am/Cm) are 2.8 and 2.6 at 25 and 35°C, respectively. This technique not only gives a high ($>10^3$) decontamination factor of americium from curium, but also removes the lanthanide fission products, La, Ce, Pr, Nd, and Pm, which remain behind in the americium fraction.

C. Final Purification of ^{242}Cm

At this stage, the ^{242}Cm is removed from the cave and separated from the LiNO_3 elutriant by a liquid-liquid extraction step using 2-ethylhexyl phenyl phosphonic acid ($\text{HEH}[\phi\text{P}]$). The final purification of the ^{242}Cm is accomplished by extraction chromatography using a column containing HDEHP adsorbed on Celite and a dilute nitric acid elutriant.⁸ Fission products Ru, Rh, La, and Ce elute from the column before the curium band and fission products Eu through Dy elute behind the curium band. This procedure also removes the last traces of alkali metal ions, alkaline earth ions, and Pu(III). The resulting ^{242}Cm in nitric acid elutriant is used directly for the preparation of the alpha sources.

III. EQUIPMENT AND REAGENTS

The equipment used for processing the sample by remote control in a high-level cave has been described previously.^{2,9,10}

The preparation of special reagents used in the liquid-liquid extraction and chromatography steps are listed below:

0.4F Aliquat-336 Nitrate in Xylene

Aliquat-336 chloride is obtained from General Mills, Inc., Kankakee, Ill. Approximately 190 ml of Aliquat-336 chloride is dissolved in analytical-grade xylene and diluted to one liter. The resultant solution is equilibrated with 2M NaNO_3 until chloride ion is undetectable in the aqueous phase when tested with AgNO_3 .

0.5F HEH[ϕ P] in Xylene

The HEH[ϕ P] is prepared by hydrolyzing 2-ethylhexylphenyl phosphonate with a 50% excess of NaOH. The neutral ester is obtained from Victor Chemical Co., Inc., Chicago Heights, Ill. A mixture of neutral phosphonate ester and NaOH is equilibrated in a stainless steel beaker for 24 hr at 97°C. The resultant sodium salt of HEH[ϕ P] is salted out of the mixture of 2-ethylhexanol and unhydrolyzed ester with an excess of xylene. Additional decontamination of the sodium salt from 2-ethylhexanol is obtained by scrubbing with xylene. The final HEH[ϕ P] is obtained by scrubbing the sodium salt with HCl, diluting with xylene, and standardizing by titration with standard NaOH solution and phenolphthalein indicator.

19 w/o Aliquat-336 Chloride-Celite

A commercial diatomaceous earth (Celite-545), obtained from Johns-Manville Co., Inc., is fractionated by the sedimentation method. The 200-400 mesh fraction is dried at 100°C for 24 hr, exposed in a desiccator to the vapors of dimethyldichlorosilane (DMCS) for one week, and dried again for one hour at 200°C. Ten grams of hydrophobic Celite are then mixed with a solution containing 2.51 g of technical-grade Aliquat-336 chloride (95%) dissolved in 50 ml of acetone. The mixture is stirred manually while the acetone is evaporated under a nitrogen stream. The resultant product contains approximately 0.4 mmol of Cl⁻ (from R₃NCH₃⁺ Cl⁻) per gram of column material.

A 10-ml bed-volume column (of 8-mm ID) is filled by gently tamping the dried Aliquat-336 chloride-Celite material into layers several millimeters thick, forming a loosely packed bed. The bed is held in place at the bottom with a coarse glass frit and at the top with a glass wool plug. The column is preconditioned with ten bed volumes of preboiled 1M HNO₃ followed by five bed volumes of 8M LiNO₃-10⁻²M HNO₃. This procedure removes all air pockets from the bed.

16 w/o HDEHP-Celite

The HDEHP-Celite column material is prepared by the same procedure as described above. Ten grams of hydrophobic Celite are mixed with 1.93 g of pure HDEHP and 50-60 ml of acetone. The acetone is evaporated under a stream of nitrogen while stirring manually. The resultant column material contains 0.50 mmol of HDEHP per gram of column material.

Column packing is carried out by the same procedure as described above. The column is preconditioned with 10 bed volumes of preboiled 0.1M HNO₃ at a rapid flow rate in order to remove all air pockets.

High-purity HNO_3 Solutions (0.3M and 0.5M)

A high-purity $\sim 15\text{M}$ HNO_3 stock solution is prepared by distillation of analytical-grade conc HNO_3 in a quartz apparatus. The 0.3M and 0.5M HNO_3 solutions are prepared from the stock solution by dilution with water from an ion-exchange column.

IV. PROCEDURE

The procedure described below was used to process ~ 230 mg of irradiated $^{241}\text{AmO}_2$ encapsulated in 18 g of aluminum. Smaller quantities of ^{241}Am were also irradiated, e.g., 120 mg of AmO_2 ; however, the procedure was essentially the same as described below except for a few changes in the quantities of reagents. A flowsheet of the procedure is shown in Figs. 1-5. The material balances of the ^{242}Cm shown throughout the flowsheet were corrected for losses due to radioactive decay.

A. Dissolution of Capsule

The dissolver solution consisted of 250 ml of 7M HNO_3 - 0.005M Hg^{+2} and 300 ml of conc ($\sim 15\text{M}$) HNO_3 . Approximately 50-ml portions of nitric acid-mercuric solution were added slowly with stirring until the liquid covered the capsule. Heat was applied to initiate the reaction. Once the capsule started to dissolve, the heat was reduced until the rate of reaction was safely under control. Additional 50-ml portions of acid solution were added when the reaction started to subside. Stirring was continued throughout the dissolving process, and the temperature was maintained at ~ 80 - 90°C .

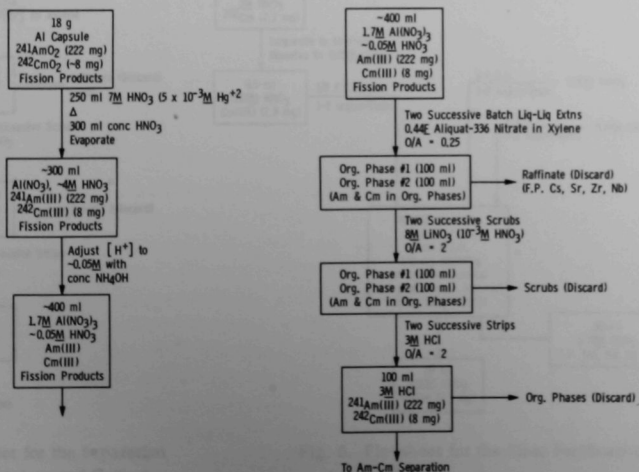


Fig. 1. Flowsheet for the Recovery of Americium and Curium from an Aluminum Capsule

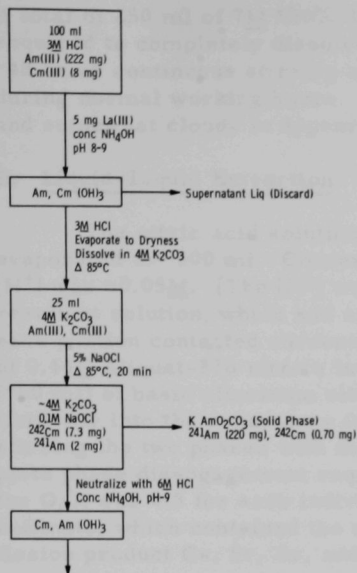


Fig. 2. Flowsheet for the Separation of Americium and Curium

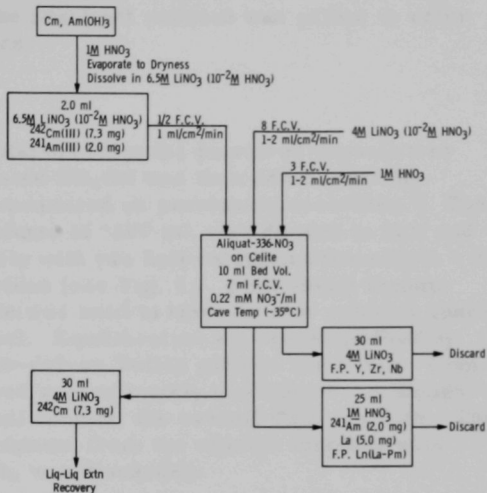


Fig. 3. Flowsheet for the Separation of Americium and Curium

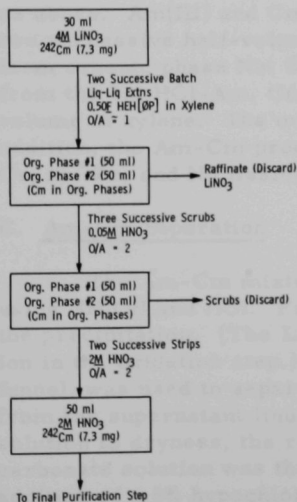


Fig. 4. Flowsheet for the Separation of Americium and Curium

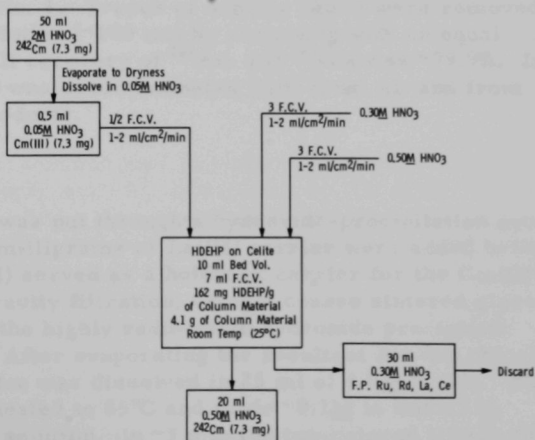


Fig. 5. Flowsheet for the Final Purification of ^{242}Cm

A total of 250 ml of 7M HNO_3 - 0.005M Hg^{+2} and 300 ml of conc HNO_3 was required to completely dissolve the capsule. The dissolution required ~48 hr of continuous stirring and heating, although acid was added only during normal working hours. The resultant solution was yellow in color and somewhat cloudy in appearance.

B. Liquid-Liquid Extraction

The nitric acid solution obtained from the dissolved capsule was evaporated to ~300 ml. Concentrated NH_4OH was then added until the $[\text{H}^+]$ was $\sim 0.05\text{M}$. (The $[\text{H}^+]$ was measured as previously described.⁹) The resultant solution, which had a volume of ~400 ml, was divided in half and each portion contacted successively with two half-volume portions ($\text{O/A} = 0.5$) of 0.44F Aliquat-336 nitrate in xylene (see Fig. 1.) A minimum amount (~50 ml) of basic aluminum nitrate was used to rinse the feed solution quantitatively into the separatory funnel. Equilibration was accomplished by stirring the two phases with motor-driven Teflon paddles for 5 min. Complete phase disengagement required approximately one minute. Although the O/A was 0.5 for each individual contact, the overall O/A was 0.25. The raffinate, which contained the aluminum from the capsule together with fission product Cs, Sr, Zr, and Nb, was discarded.

The loaded organic phases, containing the ^{241}Am and ^{242}Cm , were scrubbed successively two times with half-volume portions ($\text{O/A} = 2$) of 8M LiNO_3 - 10^{-3}M HNO_3 . The order of scrubbing was from organic phase No. 1 to No. 2. Mixing and phase disengagement times remained the same as above. Am(III) and Cm(III) were stripped from the organic phases with two successive half-volume portions of 3M HCl . The stripping order was from organic phase No. 2 to No. 1. Traces of organic phase were removed from the 3M HCl -Am, Cm solution (~100 ml) by scrubbing with an equal volume of xylene. The overall recovery of ^{241}Am and ^{242}Cm was ~99.9%. In addition, the Am-Cm product was decontaminated $>10^4$ from Al, and from Cs, Sr, Zr, and Nb fission products.

C. Am-Cm Separation

The Am-Cm mixture was put through a hydroxide-precipitation cycle using NH_4OH and HCl . Five milligrams of La(III) carrier were added before the precipitation. (The La(III) served as a holdback carrier for the Cm(III) ion in the oxidation step.) Gravity filtration, using a coarse sintered glass funnel, was used to separate the highly radioactive hydroxide precipitate from the supernatant liquid. After evaporating the resultant Am-Cm chloride solution to dryness, the residue was dissolved in 25 ml of $4.0\text{M K}_2\text{CO}_3$. The carbonate solution was then heated to 85°C and made $\sim 0.1\text{M}$ in NaOCl by addition of a 5% hypochlorite solution. In ~3 min the tan-colored KAmO_2CO_3 began to precipitate. The mixture was maintained at 85 - 90°C for 20 min, and then allowed to cool for one hour before filtering by gravity through

a coarse frit. Approximately 99% of the ^{241}Am precipitated as the slightly soluble KAmO_2CO_3 ; however, ~8-9% of the ^{242}Cm also coprecipitated with the Am(V) compound.

The ^{242}Cm plus the remaining ^{241}Am was recovered from the K_2CO_3 solution by first slowly neutralizing the carbonate with 6M HCl , precipitating the hydroxides with conc NH_4OH , and dissolving the resultant precipitate in a minimum volume of 1M HNO_3 .

The final separation of the remaining americium was performed by extraction chromatography using a column containing Aliquat-336 nitrate adsorbed on hydrophobic Celite-545. The column size and capacity are shown in Fig. 3. Feed solution for the Aliquat-336- NO_3 column was prepared by evaporating the nitric acid solution of curium to dryness and dissolving the residue in ~2 ml of 6.5M LiNO_3 - 10^{-2}M HNO_3 . Vortexing the mixture followed by brief warming aided the dissolution of the $\text{Cm}(\text{NO}_3)_3$ residue. Small portions (~2 ml) of 4M LiNO_3 - 10^{-2}M HNO_3 solution were used to rinse the load tube. A flow rate of $1-2\text{ ml/cm}^2/\text{min}$ was maintained by regulation of the nitrogen pressure applied to the top of the column. After loading, the column was eluted with 4M LiNO_3 - 10^{-2}M HNO_3 solution. During the elution the cave was darkened in order to observe the position of the curium band which was visible because of the orange luminescence associated with milligram quantities of ^{242}Cm . The first 30 ml (~3 F.C.V. + void volume) of eluate were discarded (F.C.V. -- free column volume). The ^{242}Cm eluted in the next 30 ml of eluate with the peak maximum appearing at ~5 F.C.V. (The peak maximum was approximated by measuring the total volume of eluate collected when the brightest part of the curium band eluted from the column.) From a knowledge of the separation factor, band widths, void volume, and the peak maximum of the curium band, the breakthrough point of the americium fraction was calculated.⁷ Accordingly, when a total of 8 F.C.V. (63 ml, including the void volume) of elutriant had passed through the column, the ^{241}Am was stripped from the column with 3 F.C.V. of 1M HNO_3 .

The ^{241}Am in the ^{242}Cm fraction was reduced to ~70-150 ppm by mass by the extraction chromatography column. Approximately 1% of the ^{242}Cm tailed into the ^{241}Am fraction. The 5 mg of lanthanum carrier, as well as the lanthanide fission products La through Pm, were stripped from the column along with the ^{241}Am fraction. The intense alpha activity of the ^{242}Cm produced noticeable gas pockets in the column throughout the entire path of the curium band and caused a change in the color of the column from light cream to a light gray.

At this stage of the process, the ^{242}Cm fraction was removed from the high-level cave and all additional operations were performed in a conventional glovebox. The ^{242}Cm product was recovered from the 4M LiNO_3 - 10^{-2}M HNO_3 elutriant solution by extraction with 0.5F $\text{HEH}[\phi\text{P}]$

in xylene (see Fig. 4). Separatory funnels with Teflon stopcocks were used for the extraction. The organic phases were scrubbed three successive times with 0.05M HNO_3 ($\text{O/A} = 2$). One-minute contact times were employed throughout the extractions. The ^{242}Cm was stripped from the organic phases with 2M HNO_3 . The combined strip solution was scrubbed with an equal volume of xylene to remove traces of organic phase.

D. Final Purification of ^{242}Cm

The final purification of the ^{242}Cm from any residual salts (e.g., Li, Na, and Ca) and from lanthanide fission products La-Ce and Eu-Lu was performed by extraction chromatography using a column containing HDEHP on hydrophobic Celite-545. The column size is shown in Fig. 5. Feed solution for the column was prepared by evaporating the 2M HNO_3 solution containing the ^{242}Cm to dryness. The resultant residue was dissolved in ~ 0.5 ml of 0.05M HNO_3 and loaded on the column. Two 0.5 -ml portions of 0.3M HNO_3 were used as rinse. A flow rate of $1\text{--}2$ ml/cm²/min was maintained, and the column was operated at room temperature ($\sim 25^\circ\text{C}$). After loading, the column was eluted with 3 F.C.V. of 0.30M HNO_3 . This elutrient moved the ^{242}Cm band, which was again visible due to its orange luminescence, $\sim 1/2$ the way down the column. The elutrient was then changed to 0.5M HNO_3 , which stripped the ^{242}Cm from the column in 3 F.C.V. Any Eu-Lu present remained on the column.

Losses of ^{242}Cm from this step were $< 0.3\%$. The final ^{242}Cm product was stored in an acid-leached centrifuge tube in 0.5M HNO_3 .

V. SUMMARY

Over 120 Ci of ^{242}Cm have been purified during the last three years. Routine recoveries of ^{242}Cm , disregarding losses due to radioactive decay, were $\sim 90\%$. (The majority of the 10% loss occurred during the oxidation of americium.) The resultant ^{242}Cm was radiometrically pure of all fission products and spectroscopically pure ($> 99.9\%$) of Na, Ca, Al, and Fe. In addition, the americium was reduced to ~ 100 ppm by mass, which corresponds to an alpha-activity ratio of $10^7:1$ ($^{242}\text{Cm}:^{241}\text{Am}$).

The process required approximately 10-12 normal working days for completion.

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